

## Collaborative Study of Microchemical Sulfur Determination, Using Oxygen Flask Combustion: THQ Indicator

LAVERNE H. SCROGGINS

*Eastern Regional Research Center, Agricultural Research Center, U.S. Department of Agriculture, Philadelphia, PA 19118*

A collaborative study was conducted on microchemical sulfur determination by oxygen flask combustion. Seven collaborators performed duplicate determinations on 5 samples: sulfanilamide, benzylisothiurea hydrochloride, cystine, potassium sulfate, and a mixture of potassium sulfate and phosphate. Following oxygen flask combustion, the resultant gases were absorbed in a solution containing 0.1N NaOH and 30%  $\text{H}_2\text{O}_2$ . The acidified sample was shaken 30 min and evaporated to dryness on the steam bath; the sulfate was titrated with standard barium chloride solution. The indicator used in this study was tetrahydroxyquinone. Its reliability has been previously proved and adopted by AOAC for use with the Carius-type combustion. Evaluation of the statistical data and overall consideration indicate satisfactory results for all types of compounds studied, with the exception of phosphorus-contaminated samples. Both systematic and random errors for the pure compounds were low. The method has been adopted as official first action.

The present highly successful methods adopted by the Association of Official Analytical Chemists (*Official Methods of Analysis* (1970) 11th Ed., secs. 42.027–42.030, 42.031–42.032) for the microdetermination of sulfur in organic compounds require the Carius combustion or a Pregl-type catalytic combustion assembly. These methods are time consuming, and difficulties have been encountered with certain substances, which indicate that the labile ( $>\text{SH}$ ) group and certain sulfonamides may be partially resistant to the Carius combustion. Since the discovery of the Schöniger (oxygen flask) combustion, many laboratories have turned to this time-saving process. The oxygen flask technique is convenient, because it is complete in seconds,

and its simplicity and reliability have attracted many adherents. It requires only a thick wall Erlenmeyer-type flask equipped with a solid glass stopper to which the platinum basket in which the sample is ignited can be attached. The resultant gases are immediately absorbed and oxidized in a solution present in the closed combustion flask. The resulting sulfates are, today, more generally determined volumetrically. The volumetric method employed in this study determines sulfur as sulfate with barium chloride as titrant and tetrahydroxyquinone disodium salt (THQ) as the internal indicator. This indicator changes color from yellow to orange-red. Premature formations of red barium salt, which appear as the end point is approached, disappear slowly, even with vigorous stirring. This is a pseudo end point which remains until the barium associated with the indicator finally reacts with sulfate ions. The true end point is reached when no fading of the barium indicator color occurs. This color fading must be followed continuously to prevent the selection of a pseudo end point. To facilitate end point recognition, the titration assembly (standard orange-red glass color filter comparator and a window for the sample cuvet illuminated with fluorescent light) should be used.

In this study, collaborators were asked to make duplicate determinations of the sulfanilamide, cystine, *S*-benzyl, and potassium sulfate samples forwarded to them. For the fifth set of results, they were asked to run duplicate samples with monobasic potassium phosphate added to the 2 sulfate samples prior to combustion. They were requested to use the titrimetric oxygen flask combustion method submitted to them.

## METHOD

### Sulfur

#### Oxygen Flask Combustion Method— Official First Action

(Not applicable in presence of P)

#### 47.A01

#### Reagents

(a) *Barium chloride soln.*—Approx. 0.02N. Stdze as follows: Accurately weigh 3.5–5.5 mg  $K_2SO_4$  into titrn cell, dissolve in 15 ml  $H_2O$ , add 0.15 g sulfate indicator, (f), and dissolve; dil. soln to 30 ml with alcohol. Tit. to end point (same color as ref. glass) with  $BaCl_2$  soln, making certain end point taken is real; see 47.A03. Tit. blank. Calc. factor  $F$ , mg S/ml  $BaCl_2$ .

$$F = (\text{mg } K_2SO_4 \times 0.1840) / (\text{ml } BaCl_2 - \text{ml blank}),$$

where 0.1840 is % S in  $K_2SO_4$ .

(b) *Hydrogen peroxide soln.*—30% (Fisher Scientific Co. No. H-325, or equiv. purity). (Caution: See 51.070.)

(c) *Oxygen cylinder.*—With regulator and connections for filling combustion flask.

(d) *Potassium sulfate.*—ACS, powd and dried.

(e) *Phenolphthalein soln.*—0.5% soln in 50% alcohol.

(f) *Sulfate indicator.*—Tetrahydroxyquinone (THQ) sulfate indicator (Betz Laboratories, Inc., 4636 Somerton Rd, Trevose, PA 19047) or mix 0.1 g K rhodizonate with 15 g sucrose by grinding in mortar. Vac.-dry overnight at room temp.

#### 47.A02

#### Apparatus

(a) *Mechanical shaker.*—Optional.

(b) *Oxygen flask combustion apparatus.*—Thomas-Ogg infrared igniter (Arthur H. Thomas Co. No. 6516-G10) and 500 ml thick wall combustion flask (No. 6514-F10), black sample wrappers (No. 6514-F65), Pt sample carrier, stopper, and clamp to avoid loss of sample during pressure changes which occur during combustion. App. is completely shielded within hinged cabinet. Precautions used when employing other manually operated elec. units should include proper safety shielding and reinforced gloves. Flasks must be free of org. solvs to avoid explosion.

(c) *Titration assembly.*—5 ml buret graduated in 0.01 ml, rectangular titrn cell ca  $2 \times 4 \times 5$  cm with min. capacity of 50 ml, and std orange-red glass color filter (Corning Glass Works No. 3482, CS 3-67, lantern shade yellow) selected to have

37%  $T$  at 550 nm. (Alternatively, use ref. titrn cell contg 30 ml of soln of 20 g  $Na_2Cr_2O_7/L$   $H_2O$ .) Place cell and filter side by side on milk glass window illuminated from below, preferably by fluorescent light. Mask light source so that only cells and filter are illuminated. For best results, use no overhead artificial illumination. Place microscope slides (1–3) with ground glass surface (prepd by grinding with  $H_2O$  suspension of fine SiC) over glass filter to compensate for increasing turbidity.

#### 47.A03

#### Determination

Weigh sample contg ca 0.75 mg S and fold into paper carrier. Add 5 ml 0.1N NaOH and 3 drops  $H_2O_2$  to 500 ml combustion flask. Flush flask with  $O \geq 2$  min. Place paper carrier contg sample in Pt basket, hang on hook of stopper, and insert stopper in flask. Ignite. Shake 30 min. (If gas phase has not cleared, let stand 10 min.) Open flask, and rinse stopper and Pt sample basket with  $H_2O$ . Transfer soln to 100 ml beaker, rinsing flask with min. vol.  $H_2O$ . Acidify with 2 ml 0.5N  $HNO_3$  ( $\geq 1$  ml in excess of base) and evap. to dryness on steam bath. Dissolve acid-free residue in ca 5 ml

Table 1. Collaborative results for the determination of sulfur

Coll.	Mean, %	D <sup>a</sup>	X <sup>b</sup>
Sulfanilamide, 18.58% Sulfur Theor.			
1	18.80	0.16	0.22
2	18.83	0.10	0.25
3	18.74	0.19	0.16
4	18.64	0.21	0.06
5	18.69	0.12	0.11
6	18.39	0.14	-0.19
7	18.64	0.01	0.06
Benzylisothiurea HCl, 15.82%, Sulfur Theor.			
1	15.87	0.49	0.05
2	15.80	0.04	-0.02
3	15.78	0.11	-0.04
4	15.90	0.008	0.08
5	15.67	0.15	-0.15
6	15.76	0.15	-0.06
7	15.78	0.07	-0.04
Cystine, 26.68% Sulfur Theor.			
1	26.90	0.06	0.22
2	26.74	0.23	0.06
3	26.76	0.11	0.08
4	26.88	0.01	0.20
5	26.34	0.13	-0.22
6	26.51	0.08	-0.17
7	26.64	0.03	-0.08

<sup>a</sup> D = difference between duplicate values.

<sup>b</sup> X = deviation of mean from theoretical value.

H<sub>2</sub>O and transfer to titrn cell. Rinse beaker with ca 5 ml H<sub>2</sub>O. Add 1 drop phthln and make just alk. with ca 0.1N NaOH; then acidify with ca 0.02N HNO<sub>3</sub>. Add ca 0.15 g THQ indicator, stir to dissolve, and rinse beaker 2-3 times with enough alcohol so that final soln in cell contains ca 50% alcohol. Titr. with std BaCl<sub>2</sub> soln from 5 ml buret until stable color of soln immediately after stirring matches std glass color filter. Make certain end point taken is real and not pseudo end point, which fades on standing 1-2 min (1-2 more drops BaCl<sub>2</sub> would result in over-titrn, causing soln to be definitely red). Det. blank on reagents and correct titrn values. Calc. % S, using factor *F* from 47.A01(a).

$$\% S = [(ml \text{ BaCl}_2 - ml \text{ blank}) \times F \times 100] / mg \text{ sample}$$

### Results and Recommendations

Seven collaborative laboratories reported sulfur data totaling 64 determinations for pure samples and 12 determinations for samples contaminated with phosphate ions. Three of the collaborators customarily used a THQ method routinely; 4 did not. Tables 1 and 2 contain the mean, difference between duplicate values, and the deviation of the mean from the theoretical value for each of the samples submitted. Only 4 of the 32 valued population were deviations of the mean from theoretical >0.20 and even

**Table 2. Collaborative results for the determination of sulfur potassium sulfate (18.35% sulfur theoretical)<sup>a</sup>**

Coll.	Mean, %	D <sup>a</sup>	X <sup>b</sup>
Potassium Sulfate			
1	18.50	0.01	0.13
2	18.38	0.05	0.01
3	18.36	0.04	-0.01
4	18.56	0.03	0.19
5	18.24	0.11	-0.13
6	18.44	0.10	0.07
7	18.44	0.03	0.07
Phosphate			
1	17.84	0.25	-0.53
2	22.26	0.66	3.89
3	27.56	0.31	9.19
4	16.71	0.56	-1.66
5	21.66	0.63	3.29
6	26.04	0.08	7.67

<sup>a,b</sup> See footnotes, Table 1.

these 4 values were all deviations of ≤0.25. The deviations of the mean from the theoretical value for the potassium sulfate samples were all <0.20. However, as was expected, when the samples were contaminated with phosphate, the values were not acceptable.

Within-laboratory precision, calculated from the difference between duplicates (bias) and the average deviation of the mean from theoretical values, shown in Table 3, was acceptable. All the laboratories had average values for deviation of the mean from theoretical value that were <0.20.

The statistics in Table 4 summarize the data from all 5 compounds. The overall statistical results showed acceptable standard deviations and deviations of the mean from the theoretical value for all compounds studied except for the phosphated potassium sulfates.

Evaluation of the statistical data and overall consideration shows that the oxygen flask combustion procedure for microchemical sulfur determination is a practical method, simple and rapid, with acceptable accuracy and precision.

**Table 3. Reproducibility of sulfur values among analysts, omitting sample values where "PO<sub>4</sub>" was added**

Coll.	σ <sup>a</sup>	Bias <sup>b</sup>	X <sup>c</sup>
1	0.18	0.19	0.16
2	0.09	0.08	0.08
3	0.08	0.05	0.07
4	0.08	0.13	0.13
5	0.08	-0.10	0.15
6	0.08	-0.06	0.12
7	0.03	0.01	0.06

<sup>a</sup> Standard deviation calculated from difference between duplicates for all 4 samples.

<sup>b</sup> Average deviation of mean from theoretical, observing signs.

<sup>c</sup> Average deviation of mean from theoretical, ignoring signs.

**Table 4. Summary of statistical results for the 5 samples studied**

Compound	σ <sup>a</sup>	X <sup>b</sup>	Bias <sup>c</sup>
Sulfanilamide	0.11	0.15	0.10
S-Benzyl	0.06	0.07	-0.04
Cystine	0.09	0.14	0.03
K <sub>2</sub> SO <sub>4</sub>	0.05	0.09	0.04
K <sub>2</sub> SO <sub>4</sub> + PO <sub>4</sub> <sup>3-</sup>	0.33	4.37	3.64

<sup>a-c</sup> See footnotes, Table 3.

It is, therefore, recommended that the method be adopted as official first action.

#### Acknowledgments

The Associate Referee wishes to express appreciation to the following collaborators:

C. E. Childs and T. M. Stickney, Parke Davis and Co., Ann Arbor, MI

G. M. Elsea and P. Carnes, Tennessee Eastman Co., Kingsport, TN

L. J. Frauenfelder, GAF Corp., Wayne, NJ  
H. R. Friedberg, Crobaugh Laboratories, Cleveland, OH

H. W. Galbraith and G. R. Hutchens, Galbraith Laboratories, Inc., Knoxville, TN

D. F. Ketchum and E. Lelental, Eastman Kodak Co., Rochester, NY

C. S. Yeh, Purdue University, W. Lafayette, IN

---

The recommendation of the Associate Referee was approved by the General Referee and by Subcommittee C and was adopted by the Association. Their reports will appear in (1975) *JAOAC* **58**, March issue.

---

This report of the Associate Referee was presented at the 88th Annual Meeting of the AOAC, Oct. 14-17, 1974, at Washington, DC.

Reference to brand or firm does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.